Statistical Mechanics of Semiflexible Chains:
A meanfield variational approach

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1 INTRODUCTION

The random walk model for neutral polymer is perhaps the simplest mathematical representation for long flexible chains [1]. The tremendous progress made in the theoretical understanding of conformational and dynamical properties of flexible polymer systems becomes possible because systematic calculations using the random walk model in conjunction with the inclusion of excluded volume interactions can be carried out at least in principle [2]. The resulting model, referred to as the Edwards model, is the minimal representation of real polymers that adequately describes the global properties of several polymeric systems. The random walk model views the flexible polymer chains as a Brownian curve. In the discrete representation, a flexible chain can be modeled as one for which angles between successive chain segments are not correlated. Since the orientations of chain segments are independent, the segment vectors have the Markovian property so that the mean squared end-to-end distance is proportional to the number N of segments of size a in the chain. In the continuum limit this chain becomes a Brownian curve.

In contrast there are a number of issues concerning the behavior of semiflexible chains that are not satisfactorily solved. Many polymeric molecules have internal stiffness and hence can not modeled as freely jointed chains [3]. This is especially the case in several biopolymers such as actin, DNA, and microtubules [4]. A measure of the stiffness of a polymer is in terms of the so called persistence length, l_{p}, which gives an estimate of the length scale over which the

tangent vectors along the contour of the chain backbone are correlated. The typical values of l_{p} of biopolymers lie in the range of a several nm to few mm. This range is several orders of magnitude larger than the persistence length of flexible chains. If the contour length, L, of such molecules is of the same order of magnitude as l_{p} then it is imperative to include bending rigidity to describe the conformations of the chain. In these situations the chain behaves as wormlike and the appropriate model for this was introduced sometime ago [3]. It has been known for a long time that the wormlike model provides a good starting point in the theoretical description of chains with internal stiffness. Inspired by several recent experiments [5], which have probed a number of properties of stiff biological molecules, there has been a renewed interest in understanding their shapes. The purpose of this chapter is to provide a simple way of calculating a number of interesting properties of semiflexible chains using a simple meanfield variational approach.

The effect of excluded volume profoundly changes the properties of flexible chains. Although historically the importance of excluded volume was recognized sometime ago, the introduction of the Edwards to represent the effect of this short range interaction made possible systematic calculation of various static and dynamic properties using field theoretical methods [2]. In this chapter, in which we focus on the properties of semiflexible chains, the excluded volume effects will be ignored. This is physically reasonable for relatively stiff chains for which deviations from rod-like conformations are negligible.

A simple way to account for the stiffness of a semiflexible chain is to constrain the angles between two successive segments θ to be fixed. The value of θ depends on the local stiffness of the chain. This prescription leads to the freely rotating chain model. If we describe the configurations of a polymer chain by the set of position vectors $\{\mathbf{r}_n\} = (\mathbf{r}_0, ..., \mathbf{r}_N)$ or alternatively by the set of segment vectors $\{\Delta\mathbf{r}_n\} = (\mathbf{r}_1 - \mathbf{r}_0, ..., \mathbf{r}_N - \mathbf{r}_{N-1})$, then the spatial correlation, $\langle \Delta\mathbf{r}_n \cdot \Delta\mathbf{r}_{n-1} \rangle$, in the freely rotating chain has the assigned value $a^2\cos\theta$. In the continuous limit $(a \to 0, \theta \to 0, N \to \infty, Na = L)$ the freely rotating chain becomes

the so called wormlike chain [3]. In this case, the ratio $2a/\theta^2$ defines the *persistence length* l_{p}, which is the typical length scale over which the chain changes its direction appreciably. Other conformational properties of such a model are well known in the literature [3,6-20].

The spatial correlations $\langle \Delta \mathbf{r}_n \cdot \Delta \mathbf{r}_m \rangle$, which characterize the properties of a semiflexible chain, decay exponentially as $\exp[-a|n-m|/l_{\mathrm{p}}]$. Thus the conformational properties of a semiflexible chain beyond the length scale l_{p} reduce to those of flexible chains, i.e., one can view the stiff chain as being made up of several rigid segments of length l_{p} that are freely joined. However because of the intrinsic skeletal stiffness of many synthetic polymers as well as biopolymers one needs to develop a model that explicitly builds effects due to chain bending. The chain stiffness turns out to be a relevant parameter in the description of isotropic-nematic transition condition in liquid-crystalline polymers [15]. Even for an isolated chain, the chain stiffness should be taken into account to describe the local properties of stiff polymer chains. This is especially important in polyelectrolytes. The scaling behavior of the electrostatic persistence length l_{e} is known to depend on the rigidity of the chain [16, 17]. Many biological molecules and short chains of otherwise flexible chains also belong to the class for which the chain stiffness plays an important role.

A number of theoretical models have been introduced in the literature to account for chain stiffness. The earliest model for stiff chains is the wormlike chain (also known as Kratky-Porod model) in which the angles between successive chains are constrained [3]. Although physically reasonable, this model has not yielded analytically tractable results for equilibrium and dynamical properties. Harris and Hearst introduced a "simplified model" of stiff chains in which the tangent vector $\mathbf{u}(s) = \partial \mathbf{r}/\partial s$ was allowed to fluctuate as opposed to having the constraint $\mathbf{u}^2(s) = 1$ for all s [7]. It has been noted that the resulting model does not satisfy the spatial homogeneity of stiff chains. More recently a model that does not suffer from this restriction was proposed by Lagowski, Noolandi, and Nickel [18] using a functional integral formalism. These authors showed that the resulting model yielded the

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mean squared end-to-end distance in agreement with Kratky-Porod. The spatial correlations decay exponentially with a slightly shorter value of the persistence length.

In this chapter we show that a model for stiff chains proposed by Lagowski, Noolandi and Nickel (LNN) [18] results from a stationary phase evaluation of certain functional integrals that occur in an appropriate field theory for stiff chains. Our approach is systematic and can be applied to many diverse problems involving semiflexible chains. We should note that Winkler et al. [19] have also obtained a model for stiff chains using the maximum entropy principle. These authors did not notice that their model in the continuum limit is identical to that of LNN. Furthermore their method appears more cumbersome than the standard functional integral approach presented here.

The rest of the chapter is organized as follows. In section 2, we present the basic strategy behind the meanfield variational approach. The resulting model, as mentioned earlier, leads to the LNN representation of wormlike chains. The theoretical ideas are used to calculate the distribution of end-to-end distance in semiflexible chains in section 3. The application of the theory to the problem of semiflexible chains under tension with forces or the stretching of DNA is developed in section 4. The possible limitations of the theory are illustrated in section 5 by studying the behavior of semiflexible chains in a stretching nematic field. The chapter is concluded in section 6 with a few additional remarks.

2 MEANFIELD MODEL

2.1 flexible chains

The basic methodology can be illustrated using the simpler example of a flexible chain. This is the limiting case of a stiff chain as the rigidity vanishes. The probability function for

the flexible chain conformations without excluded volume interactions can be written as

$$\Psi\{\mathbf{r}_n\} = \prod_{n=1}^{N} \psi(\Delta\mathbf{r}_n) \tag{1}$$

where $\psi = \delta(|\Delta\mathbf{r}| - a)/4\pi a^2$ denotes the random distribution of a segment vector of length a. Eq. (1) accounts for the chain connectivity. We can rewrite the probability weight in Eq. (1) by introducing auxiliary fields λ_n as

$$\Psi\{\mathbf{r}_n\} \propto \int_{-i\infty}^{i\infty} \prod_{n=1}^{N} \mathrm{d}\lambda_n \, \exp\left[-\sum_{n=1}^{N} \frac{\lambda_n}{a}((\Delta\mathbf{r}_n)^2 - a^2)\right]. \tag{2}$$

We now show that a stationary phase evaluation of the free energy of the chain described by above weight leads to the probability weight for the Brownian chain. This approximation amounts to relaxing the locally enforced constraint of $(\Delta\mathbf{r}_n)^2 = a^2$ to a global one, $\langle(\Delta\mathbf{r}_n)^2\rangle = a^2$, and the validity of the approximation can be justified *a posteriori* as $a \to 0$. The free energy F of a non-interacting flexible chain can be written as

$$\exp(-F/k_\mathrm{B}T) = \mathrm{const} \int_{-i\infty}^{i\infty} \prod_{n=1}^{N} \mathrm{d}\lambda_n \exp(-\mathcal{F}\{\lambda_n\}) \tag{3}$$

where the free energy functional $\mathcal{F}\{\lambda_n\}$ is defined by

$$\begin{aligned}
\mathcal{F}\{\lambda_n\} &\equiv -\ln\left\{\int \prod_{n=1}^{N} \mathrm{d}\mathbf{r}_n \exp\left[-a^{-1}\sum_{n=1}^{N} \lambda_n \mathbf{r}_n^2\right]\right\} - a\sum_{n=1}^{N} \lambda_n \\
&= \sum_{n=1}^{N} \left(\tfrac{3}{2}\ln\lambda_n - \lambda_n a\right) + \mathrm{const}. \tag{4}
\end{aligned}$$

In the above equation, the order of the $\mathbf{r}_n$ and λ_n integrations is interchanged. If we denote the trajectory λ_n along which the integrand in Eq. (3) has its maximum value by λ_n^{cl}, then the free energy can be expanded around this stationary phase trajectory, λ_n^{cl}. In the following the subscript 'cl' will be omitted. In the meanfield theory for which the constraint is imposed only on an average, we retain only the leading term in this expansion. By setting the partial derivative of the free energy functional $\mathcal{F}\{\lambda_n\}$ with respect to λ_n to zero, we get the stationary phase condition:

$$\frac{\partial}{\partial\lambda_n}\mathcal{F}\{\lambda_n\} = 0 \Rightarrow \lambda_n = \frac{3}{2a}, \qquad 0 \leq n \leq N. \tag{5}$$

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The independence of λ_n on n reflects the symmetry of the problem of an ideal flexible chain. Since the delta function can be also represented as

$$\delta(\mathbf{r}) = \lim_{a \to 0} \Big(\frac{3}{2\pi a^2}\Big)^{3/2} \exp(-\mathbf{r}^2/2a^2), \tag{6}$$

the stationary phase evaluation becomes very accurate in the continuum limit, $a \to 0$. Thus long flexible chains, i.e., $N \gg 1$ can be well described by the following weight in the continuum limit

$$\Psi_{\mathrm{MF}}[\mathbf{r}(s)] \propto \exp\Big[-\frac{3}{2a} \int_0^L ds \Big(\frac{\partial \mathbf{r}}{\partial s}\Big)^2\Big] \tag{7}$$

where $\Psi[\mathbf{r}(s)]$ is written in the functional integral notation and is the Wiener measure.

By treating the random fields $\lambda(s)$ at the mean field level, the microscopic constraints conjugate to the fields $\lambda(s)$, which ensure that the chain segments are connected but otherwise randomly distributed, are relaxed to the global ones. This results in the expected probability weight given in Eq. (7) for a long flexible chain and is the Wiener measure obtained in the path integral description of a diffusion equation.

2.2 Linear stiff chains

The approach described above can be extended to semiflexible chains. In this calculation we assume that the stretching of two connected chain segments is not important so that the coupling between this degree of freedom and the bending degree of freedom can be ignored [20]. In this case, the weight in Eq. (1) needs to be modified so that it yields non-vanishing correlations $\langle \Delta \mathbf{r}_n \cdot \Delta \mathbf{r}_{n-1} \rangle = a^2 \theta^2 = 2a^3/l_{\mathrm{p}}$. This can be achieved if we multiply the weight in Eq. (1) by the Boltzmann weight $\exp(l_{\mathrm{p}} a^{-3} \sum_{n=1}^{N-1} \Delta \mathbf{r}_{n+1} \cdot \Delta \mathbf{r}_n)$ corresponding to the local interactions between adjacent segments. This term favors parallel alignment of adjacent segments over bent configurations. In the λ_n representation of the probability weight, this can be rewritten as $\exp[-\frac{1}{2}l_{\mathrm{p}} a^{-3} (\Delta \mathbf{r}_{n+1} - \Delta \mathbf{r}_n)^2]$ with a redefinition of λ_n. Then the weight

associated with a particular configuration of a semiflexible chain becomes

$$\Psi\{\mathbf{r}_n\} \propto \int_{-i\infty}^{i\infty} \prod_{n=1}^{N} \mathrm{d}\lambda_n \, \exp\left[-\sum_{n=1}^{N} \frac{\lambda_n}{a}((\Delta\mathbf{r}_n)^2 - a^2) - \frac{l_{\mathrm{p}}}{2a^3} \sum_{n=1}^{N-1}(\Delta\mathbf{r}_{n+1} - \Delta\mathbf{r}_n)^2\right]. \quad (8)$$

In the continuum limit, this can be written as functional integral

$$\Psi[\mathbf{u}(s)] \propto \exp\left[-\frac{l_{\mathrm{p}}}{2}\int_0^L \mathrm{d}s\left(\frac{\partial\mathbf{u}}{\partial s}\right)^2\right] \prod_{0 \leq s \leq L} \delta(\mathbf{u}^2(s) - 1) \quad (9)$$

where $\mathbf{u}(s) \equiv \partial\mathbf{r}(s)/\partial s$ is a unit tangent vector. The properties associated with the weight $\Psi[\mathbf{u}(s)]$ are well known in the literature [2-3,10]. The random variable $\mathbf{u}(s)$ describes the rotational Brownian motion on a unit sphere, $\mathbf{u}^2 = 1$. If we let $P(\mathbf{u}_s, \mathbf{u}_{s'}; s', s)$ be the probability that $\mathbf{u}(s') = \mathbf{u}_{s'}$ when $\mathbf{u}(s) = \mathbf{u}_s$, then this function obeys a diffusion equation on the unit sphere. The solution of the diffusion equation can be expanded in terms of spherical harmonics. This enables us to compute the following correlation

$$\langle\mathbf{u}(s') \cdot \mathbf{u}(s)\rangle = \exp(-|s' - s|/l_{\mathrm{p}}). \quad (10)$$

This correlation along with the Markovian property of $\mathbf{u}$ leads to the mean squared end-to-end distance given by

$$\begin{aligned}
\langle R^2 \rangle &= \int_0^L \int_0^L \mathrm{d}s\,\mathrm{d}s' \langle\mathbf{u}(s') \cdot \mathbf{u}(s)\rangle \\
&= 2l_{\mathrm{p}}L - 2l_{\mathrm{p}}^2(1 - \mathrm{e}^{-L/l_{\mathrm{p}}}). \quad (11)
\end{aligned}$$

Even though the results given in Eq. (10) and Eq. (11) are exact, the use of Eq. (9) to describe non-ideal semiflexible chains turns out to be quite formidable. The major difficulty arises because of the constraint $\mathbf{u}^2(s) = 1$. One encounters similar difficulty in other physical systems described by the non-linear σ model [21] for which the magnitude of a spin $\mathbf{S}$ is held fixed, $\mathbf{S}^2 = \text{const}$. Thus it is of practical interest to obtain a tractable model for such constrained systems. We will extend the stationary phase approach adopted for the flexible chain to obtain a tractable meanfield model for a semiflexible chain.

In our stationary phase approach, the field λ_n is treated as a parameter to be determined. The dependence of λ_n on n depends on the problem under consideration. The free energy

functional for an ideal semiflexible chain can be written as

$$\mathcal{F}\{\lambda_n\} = -\ln \int \prod_{n=1}^{N} d\mathbf{r}_n \, \exp\left[-\frac{E}{k_B T} + a \sum_{n=1}^{N} \lambda_n\right] \tag{12}$$

where E in a matrix form is given by

$$\frac{Ea}{k_B T} = \zeta^T Q \zeta \tag{13}$$

with $\zeta \equiv \{\mathbf{r}_1, ..., \mathbf{r}_N\}^T$. The $3N \times 3N$ matrix Q is defined by

$$Q_{nm} = \lambda_n \delta_{n\ m} - \frac{l_p}{2a^2}(1 + \delta_{n\ m\pm 1}). \tag{14}$$

Then the free energy $\mathcal{F}$ is given by

$$\mathcal{F}\{\lambda_n\} = \frac{3}{2} \ln(\det Q) - a \sum_{n=1}^{N} \lambda_n + \text{const.} \tag{15}$$

The stationary phase evaluation of λ_n amounts to minimizing the free energy with respect to λ_n, i.e.,

$$\frac{\partial}{\partial \lambda_n}\mathcal{F}\{\lambda_n\} = 0 \Rightarrow \frac{3}{2}\frac{\partial \ln(\det Q)}{\partial \lambda_n} = a, \qquad 1 \leq n \leq N. \tag{16}$$

It can be easily shown that the minimization condition in Eq. (16) amounts to requiring $\langle \mathbf{u}^2 \rangle = 1$ in the continuous limit. This follows because Eq. (16) can be rewritten as $\frac{\partial}{\partial \lambda_n}\mathcal{F} = \langle (\Delta \mathbf{r}_n)^2/a^2 \rangle - 1$. This is a simultaneous equation for the unknown parameters λ_n for which we can not find an analytical solution. An examination of the structure of the matrix Q, however, leads to the following properties of λ_n which satisfy the above equation; $\lambda_1 = \lambda_N \neq \lambda_2 =, ..., = \lambda_{N-1}$. For our purposes it suffices if λ_n can be chosen so that $\langle \mathbf{u}^2(s) \rangle = 1$ and other conformational properties are reproduced. If all λ_n are equal to each other, as is the case for the flexible chain, then the chain described by the probability weight in Eq. (8) shows inhomogeneity, i.e., the chain fluctuates more strongly at both ends than elsewhere. Having recognized the translational asymmetry in the problem of a semiflexible chain, it is convenient to rewrite λ_n as follows; $\lambda_1 = \lambda_N = \lambda + \delta/a$, $\lambda_n = \lambda$ $(2 \leq n \leq N - 1)$. With

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these simplifications, the weight for the semiflexible chain at the level of a stationary phase approximation, becomes

$$\Psi_{\mathrm{MF}}[\mathbf{u}(s)] \propto \exp\left[-\lambda \int_0^L \mathrm{d}s \mathbf{u}^2(s) - \frac{l_{\mathrm{p}}}{2} \int_0^L \mathrm{d}s \left(\frac{\partial \mathbf{u}}{\partial s}\right)^2 - \delta(\mathbf{u}_0^2 + \mathbf{u}_L^2)\right]. \tag{17}$$

The functional in Eq. (17) is identical in form to that proposed by LNN. The explicit expression for $\det Q$ and thus the stationary-point conditions for λ and δ can be obtained by setting a recursion relation in N. Alternatively, we can exploit an analogy between the path integral in Eq. (17) and the harmonic oscillator in quantum mechanics [22]. The propagator of a harmonic oscillator of a mass l_{p} and a frequency $\Omega = \sqrt{2\lambda/l_{\mathrm{p}}}$, denoted by $Z(\mathbf{u}_0, \mathbf{u}_L; L)$, is given by

$$Z(\mathbf{u}_0, \mathbf{u}_L; L) = \left(\frac{2\pi \ \sinh \Omega L}{\Omega l_{\mathrm{p}}}\right)^{3/2} \exp\left[-\frac{(\mathbf{u}_L^2 + \mathbf{u}_0^2) \cosh \Omega L - 2\mathbf{u}_0 \cdot \mathbf{u}_L}{\Omega l_{\mathrm{p}}/2 \cdot \ \sinh \Omega L}\right]. \tag{18}$$

We can thus rewrite the free energy as

$$
\begin{aligned}
\mathcal{F}[\lambda, \delta] &= -\ln \int \mathrm{d}\mathbf{u}_0 \mathrm{d}\mathbf{u}_L \ \mathrm{e}^{-\delta(\mathbf{u}_0^2 + \mathbf{u}_L^2)} \ Z(\mathbf{u}_0, \mathbf{u}_L; L) - (L\lambda + 2\delta) + \mathrm{const} \\
&= \tfrac{3}{2} \ln\left[\left(\delta \ \sinh L \sqrt{\frac{2\lambda}{l_{\mathrm{p}}}} + \sqrt{\frac{\lambda l_{\mathrm{p}}}{2}} \cosh L \sqrt{\frac{2\lambda}{l_{\mathrm{p}}}}\right)^2 - \frac{\lambda l_{\mathrm{p}}}{2}\right] \\
&\quad - \tfrac{3}{2} \ln \sqrt{\frac{\lambda l_{\mathrm{p}}}{2}} - \tfrac{3}{2} \ln\left(\sinh L \sqrt{\frac{2\lambda}{l_{\mathrm{p}}}}\right) - (L\lambda + 2\delta) + \mathrm{const} \tag{19}
\end{aligned}
$$

where we have used

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mathrm{d}x \ \mathrm{d}y \mathrm{e}^{-p^2(x^2 + y^2) \pm qxy} = \frac{\pi}{\sqrt{p^4 - \frac{1}{4}q^2}}. \tag{20}$$

A little algebra leads to the following stationary phase conditions for λ and δ which require $\frac{\partial}{\partial \lambda}\mathcal{F} = 0 = \frac{\partial}{\partial \delta}\mathcal{F}$:

$$\sqrt{\frac{\lambda l_{\mathrm{p}}}{2}} = \delta = \frac{3}{4} \tag{21}$$

Note here that the values of λ and δ don't depend on the contour length L of a chain. Since the stationary phase condition is imposed on λ, only one of l_{p} or λ is independent.

To understand the features implied by the weight in Eq. (17), let us compute the correlation $\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle$. Using the Markovian property of $\mathbf{u}$, the correlation can be computed:

$$
\begin{aligned}
\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle &= \mathcal{N}^{-1} \int \mathcal{D}[\mathbf{u}] \ \mathbf{u}(s) \cdot \mathbf{u}(s') \ \Psi_{\mathrm{MF}}[\mathbf{u}] \\
&= \mathcal{N}^{-1} \int \mathrm{d}\mathbf{u}_0 \mathrm{d}\mathbf{u}_s \mathrm{d}\mathbf{u}_{s'} \mathrm{d}\mathbf{u}_L \mathrm{e}^{-\delta(\mathbf{u}_0^2 + \mathbf{u}_L^2)} Z(\mathbf{u}_L, \mathbf{u}_{s'}; L - s') \\
&\quad \times Z(\mathbf{u}_{s'}, \mathbf{u}_s; s' - s) \mathbf{u}(s) \cdot \mathbf{u}(s') Z(\mathbf{u}_s, \mathbf{u}_0; s) \\
&= \frac{\partial}{\partial \alpha}\bigg|_{\alpha=0} \ln\bigg[\int \mathrm{d}\mathbf{u}_s \mathbf{u}_{s'} \mathrm{e}^{-\delta(\mathbf{u}_s^2 + \mathbf{u}_{s'}^2) + \alpha \mathbf{u}_s \cdot \mathbf{u}_{s'}} Z(\mathbf{u}_{s'}, \mathbf{u}_s; s' - s)\bigg] \\
&= \exp(-|s' - s|/l_0) \tag{22}
\end{aligned}
$$

where $\mathcal{N}$ is the normalization constant given by $\mathcal{N} = \int \mathcal{D}[\mathbf{u}] \ \Psi_{\mathrm{MF}}[\mathbf{u}]$ and $l_0 \equiv \frac{2}{3} l_{\mathrm{p}}$. A direct consequence of the above correlation is $\langle \mathbf{u}^2 \rangle = 1$ and thus the constraint $\mathbf{u}^2 = 1$ is enforced only on an average in the meanfield model of semiflexible chains with the weight given in Eq. (17). The above correlation can be compared with one in Eq. (10) obtained with the exact weight. A comparison of Eq. (10) and Eq. (22) shows that the persistence length for the approximate model for stiff chains (cf. Eq. (17)) is smaller by a factor of $\frac{2}{3}$. The plausible reason for this is the following: In the original model the constraint condition is $\mathbf{u}^2(s) = 1$ for all values of s. The model obtained by enforcing the global condition $\langle \mathbf{u}^2 \rangle = 1$ allows for unrestricted (restricted only on an average) fluctuations in $\mathbf{u}$ thus allowing for configurations that would be prohibited by the restricted condition $\mathbf{u}^2(s) = 1$. Thus we would expect l_0 to be less than l_{p}.

Winkler et al. [19] have obtained exactly the same result (see their Eq. (4.18)) using the maximum entropy principle. Since they also only enforce the constraint on an average the resulting theory, as described here, should be viewed as meanfield like. If l_0 is understood as a new definition of the persistence length, then the stationary phase weight in Eq. (17) predicts the same conformational behavior as the exact one in Eq. (9). If dimension d is large enough, we expect the effect of fluctuations around the mean value to become minimal. It is known that the stationary phase approach described here becomes exact as $d \to \infty$ [18]. It's worth noting that for a chain described by this weight with $\delta = 0$, the above corre-

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lation holds only for $0 \ll s, s' \ll L$. This is because of the excess end fluctuations in this case.

2.3 Closed stiff chains

For practical purposes it's more convenient to use a translationally symmetric model for a semiflexible chain, i.e., one described by $\Psi_{\mathrm{MF}}[\mathbf{u}(s)]$ in Eq. (17) with $\delta = 0$. For ring polymers for which the periodic condition $\mathbf{u}(0) = \mathbf{u}(L)$ and the closure relation $\int_0^L \mathbf{u}(s)\mathrm{d}s = 0$ are imposed, we expect all the $\lambda(s)$ to be equal or $\lambda(s)$ should be independent of s. The free energy in this case can be written as

$$\mathcal{F}[\lambda] = -\ln \int_{\mathbf{u}_0=\mathbf{u}_L} \mathcal{D}[\mathbf{u}(s)]\delta(\int_0^L \mathrm{d}s\ \mathbf{u}(s))\Psi_{\mathrm{MF}}[\mathbf{u}(s)]\big|_{\delta=0} - L\lambda. \tag{23}$$

To compute this integral, it is convenient to introduce the Fourier transform

$$\mathbf{u}(s) = \sum_{n=-\infty}^{\infty} \mathbf{u}_n \exp\left[i\frac{2\pi s n}{L}\right]. \tag{24}$$

Completeness of this expansion is reflected in the closure condition

$$\frac{1}{L}\int \mathrm{d}s\ \exp\left[i\frac{2\pi s}{L}(n' - n)\right] = \delta_{nn'}. \tag{25}$$

In terms of new variables $\mathbf{u}_n$, the weight can be written as

$$\Psi_{\mathrm{MF}}\{\mathbf{u}_n\} = \exp\left\{-\sum_{n\neq 0}\left[\frac{l_\mathrm{p}}{2}\frac{(2\pi n)^2}{L} + \lambda L\right]\mathbf{u}_n \cdot \mathbf{u}_{-n}\right\} \tag{26}$$

where the contribution from $n = 0$ is excluded to incorporate the closure condition $\int_0^L \mathbf{u}(s)\mathrm{d}s = 0$. Consequently free energy becomes

$$\mathcal{F}[\lambda] = -\ln \int \prod_{n\neq 0} \mathrm{d}\mathbf{u}_n \left|\det\frac{\partial \mathbf{u}(s)}{\partial \mathbf{u}_n}\right| \Psi_{\mathrm{MF}}\{\mathbf{u}_n\} - L\lambda. \tag{27}$$

Since the transformation in Eq. (24) linear, the Jacobi determinant $\left|\det\frac{\partial \mathbf{u}(s)}{\partial \mathbf{u}_n}\right|$ is independent of $\mathbf{u}_n$. Furthermore it does not depend on λ. Its value is thus unimportant and will give rise

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to an additive constant to the free energy:

$$
\begin{aligned}
\mathcal{F}[\lambda] &= -\ln \int \prod d\mathbf{u}_n \Psi_{\mathrm{MF}}\{\mathbf{u}_n\} - L\lambda + \mathrm{const.} \\
&= \tfrac{3}{2} \sum_{n\neq 0} \ln\left(1 + \frac{\lambda L^2}{2l_{\mathrm{p}} n^2 \pi^2}\right) + \mathrm{const.} \\
&= 3 \ln\left(\sinh L \sqrt{\frac{\lambda}{2l_{\mathrm{p}}}}\right) - \tfrac{3}{2}\ln(L\lambda) - L\lambda + \mathrm{const.}
\end{aligned}
\tag{28}
$$

where const. refers to λ-independent terms. In the last step of the above equation, we have used

$$
\ln \sinh x = \ln x + \sum_{n=1}^{\infty} \ln\left(1 + \frac{x^2}{n^2 \pi^2}\right).
\tag{29}
$$

Now the stationary phase condition reads

$$
\sqrt{\frac{l_{\mathrm{p}}\lambda}{2}} = \tfrac{3}{4}\left(\coth L \sqrt{\frac{\lambda}{2l_{\mathrm{p}}}} - \frac{1}{L}\sqrt{\frac{2l_{\mathrm{p}}}{\lambda}}\right).
\tag{30}
$$

Here we have L-dependent condition for λ. This is because only paths which satisfy the cyclic conditions, $\mathbf{u}(L) = \mathbf{u}(0)$ and $\int_0^L \mathbf{u}(s)\mathrm{d}s$, contribute to the free energy $\mathcal{F}$. The cyclic conditions are also incorporated in the correlation of $\mathbf{u}(s)$, i.e.,

$$
\begin{aligned}
\langle \mathbf{u}(s') \cdot \mathbf{u}(s)\rangle &= \sum_{n,n'\neq 0} \langle \mathbf{u}_n \cdot \mathbf{u}_{n'}\rangle \exp\left[i\frac{2\pi}{L}(s'n' + sn)\right] \\
&= \tfrac{3}{2} \sum_{n\neq 0} \frac{\exp\left[i\frac{2\pi n}{L}(s'-s)\right]}{\lambda L + \frac{l_{\mathrm{p}}}{2}\frac{(2\pi n)^2}{L}}
\end{aligned}
\tag{31}
$$

where $\langle ...\rangle$ is defined by

$$
\langle \mathbf{u}_n \cdot \mathbf{u}_{n'}\rangle = \frac{\int \prod_{n\neq 0} d\mathbf{u}_n \mathbf{u}_n \cdot \mathbf{u}_{n'} \Psi_{\mathrm{MF}}\{\mathbf{u}_n\}}{\int \prod_{n\neq 0} d\mathbf{u}_n \Psi_{\mathrm{MF}}\{\mathbf{u}_n\}}.
\tag{32}
$$

Upon using the following identity

$$
\sum_{n=1}^{\infty} \frac{\cos nx}{n^2 + \alpha^2} = \frac{\pi}{2\alpha} \cdot \frac{\cosh \alpha(\pi - x)}{\sinh \alpha\pi} - \frac{1}{2\alpha^2}
\tag{33}
$$

we can rewrite the correlation of the unit tangent vectors in a closed form

$$
\langle \mathbf{u}(s') \cdot \mathbf{u}(s)\rangle = \frac{\cosh[\Omega(L - 2|s'-s|)/2] - 2/\Omega L \cdot \sinh(\Omega L/2)}{\cosh(\Omega L/2) - 2/\Omega L \cdot \sinh(\Omega L/2)}.
\tag{34}
$$

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Note here that $\langle \mathbf{u}(s+L) \cdot \mathbf{u}(s) \rangle = \langle \mathbf{u}^2(s) \rangle = 1$. In the limit of $L \to \infty$, however, the cyclic conditions are irrelevant. That is the stationary phase condition and the correlation given above reduce to those of open chains. This can be checked by taking the limit $L \to \infty$ in above equations for the ring polymers. An alternative method (without derivation) for ring segments has been proposed earlier [23]. This involves modifying the original Harris-Hearst model for open chains. Huber et al. have computed quasi-elastic scattering for a modified version of this model [24].

2.4 Linear periodic chains

The ring polymer described by Eq. (26) was introduced to circumvent difficulties associated with inhomogeneity in the linear chain with a uniform stationary phase value λ. According to the correlation function in Eq. (31), however, we can assume a uniform λ even for the chains with periodic boundary conditions only without violating the homogeneity of the chain. In this case we should include $n = 0$ contribution in the Fourier modes; the free energy is thus given by

$$\mathcal{F}[\lambda] = 3 \ln \left(\sinh L \sqrt{\frac{\lambda}{2l_{\mathrm{p}}}} \right) - L\lambda + \mathrm{const.} \tag{35}$$

This leads to the following stationary phase condition

$$\sqrt{\frac{l_{\mathrm{p}}\lambda}{2}} = \tfrac{3}{4} \coth L \sqrt{\frac{\lambda}{2l_{\mathrm{p}}}}. \tag{36}$$

The periodic boundary condition is also incorporated in the correlation function which reads

$$\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle = \frac{\cosh[(L - 2|s' - s|)\Omega/2]}{\cosh(\Omega L/2)}. \tag{37}$$

This correlation shows that the chain with periodic boundary condition is homogeneous; $\langle \mathbf{u}^2(s) \rangle = 1$ for all s, $0 \le s \le L$. As $L \to \infty$, the periodic boundary condition is irrelevant as in the ring polymers.

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An alternative and useful presentation of this calculation can be made writing the curvature term in a symmetric way. Due to the periodic boundary conditions, i.e., $\mathbf{u}(0) = \mathbf{u}(L)$ and $\frac{\partial}{\partial s}\mathbf{u}(0) = \frac{\partial}{\partial s}\mathbf{u}(L)$, the free energy functional for the semiflexible chain can be written as

$$\mathcal{F}[\lambda] = -\ln \int \mathcal{D}\mathbf{u}(s)\exp\left[-\tfrac{1}{2}\int_0^L\int_0^L \mathrm{d}s\mathrm{d}s'\mathbf{u}(s)Q(s,s')\mathbf{u}(s)\right] - \int \mathrm{d}s\lambda(s) \tag{38}$$

where the operator Q is defined by

$$Q(s,s') = \left[-l_\mathrm{p}\left(\frac{\partial}{\partial s}\right)^2 + 2\lambda(s)\right]\delta(s'-s). \tag{39}$$

Integration with respect to $\mathbf{u}(s)$ leads to

$$\mathcal{F}[\lambda] = \tfrac{3}{2}\,\mathrm{tr}\,\ln Q - \int \mathrm{d}s\lambda(s). \tag{40}$$

The stationary phase condition can be obtained by requiring $\partial\mathcal{F}/\partial\lambda(s) = 0$:

$$1 = \tfrac{3}{2}\left(\frac{2}{Q}\right)_{s,s} = \tfrac{3}{2}\left(\frac{1}{-\frac{l_\mathrm{p}}{2}\frac{\partial^2}{\partial s'^2} + \lambda(s')}\right)_{s,s}. \tag{41}$$

If a uniform stationary phase value λ is assumed, the above equation can be Fourier transformed. To this end, it is convenient to define a complete set of eigenstates $\{|s\rangle\}$ with s a curvilinear space label, and a complete set $\{|n\rangle\}$, Fourier-conjugate to this, such that $\frac{\partial}{\partial s}|n\rangle = i\frac{2\pi n}{L}|n\rangle$. Thus $|s\rangle$ and $|n\rangle$ are related with each other through $\langle n|s\rangle = \frac{1}{\sqrt{L}}\exp[i\frac{2\pi ns}{L}]$. With the aid of these, the right hand side of the above equation can be written as

$$\begin{aligned}
\tfrac{3}{2}\left(\frac{1}{-\frac{l_\mathrm{p}}{2}\frac{\partial^2}{\partial s'^2} + \lambda}\right)_{s,s} &= \tfrac{3}{2}\langle s|\left(\frac{1}{-\frac{l_\mathrm{p}}{2}\frac{\partial^2}{\partial s'^2} + \lambda}\right)|s\rangle \\
&= \tfrac{3}{2}\sum_{n=-\infty}^{\infty}\langle s|\left(\frac{1}{-\frac{l_\mathrm{p}}{2}\frac{\partial^2}{\partial s'^2} + \lambda}\right)|n\rangle\langle n|s\rangle \\
&= \tfrac{3}{2}\sum_{n=-\infty}^{\infty}\frac{1}{\lambda L + \frac{l_\mathrm{p}}{2}\frac{(2\pi n)^2}{L}}. \tag{42}
\end{aligned}$$

Combined with the identity in Eq. (33), the stationary phase condition relation can be rewritten as

$$\sqrt{\frac{l_\mathrm{p}\lambda}{2}} = \tfrac{3}{4}\,\coth L\sqrt{\frac{\lambda}{2l_\mathrm{p}}}. \tag{43}$$

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This condition becomes the same one as in Eq. (21). The model described by Eq. (35) with $L \to \infty$ leads to the same result for the stationary phase condition and correlation of $\mathbf{u}(s)$ as the previous one in Eq. (17). In section 4, we adopt this approach to examine the elastic response of a semiflexible chain under tension.

2.5 Operator representations

For periodic chains, we can exploit the analogy with quantum mechanics and use an operator representation of the free energy. This is especially useful as $L \to \infty$ which allows the use of ground state dominance approximation. If we interpret $\hat{\mathbf{p}} \equiv l_{\mathrm{p}} \frac{\partial}{\partial s} \mathbf{u}$ as the momentum operator and $\hat{\mathbf{u}}$ as the position operator such that they satisfy the commutation relation $[\hat{p}_j, \hat{u}_k] = -i\delta_{jk}$, the free energy of periodic chain can be written as [25]

$$\mathcal{F}[\lambda] = -\ln \, \mathrm{tr} \, e^{-L\hat{\mathcal{H}}[\lambda]} - L\lambda \tag{44}$$

where the Hamiltonian $\hat{\mathcal{H}}$ is defined by

$$\hat{\mathcal{H}}[\lambda] = \frac{\hat{\mathbf{p}}^2}{2l_{\mathrm{p}}} + \lambda\hat{\mathbf{u}}^2. \tag{45}$$

This problem is equivalent to a 3-dimensional quantum harmonic oscillator moving in imaginary time $s = -it$; if we denote the energy eigenvalues of the Hamiltonian in Eq. (45) by $E_{\mathbf{n}}$ with $\mathbf{n} = (n_1, n_2, n_3)$ and $n_i = 0, 1, 2...$, then

$$\begin{aligned}
\mathrm{tr} \, e^{-L\hat{\mathcal{H}}[\lambda]} &= \sum_{n_1,n_2,n_3=0}^{\infty} e^{-LE_{\mathbf{n}}} \\
&= \left(\sum_0^{\infty} e^{-L\Omega(n+\frac{1}{2})} \right)^3 \\
&= \left(\frac{1}{2\sinh(\frac{1}{2}\Omega L)} \right)^3.
\end{aligned} \tag{46}$$

This calculation gives the same stationary phase condition as before.

This approach is especially useful as $L \to \infty$. For large L, we can use the following formula [25]

$$\mathrm{e}^{-L\hat{\mathcal{H}}} = \mathrm{e}^{-LE_0}\Big[|0\rangle\langle 0| + \mathcal{O}\big(\mathrm{e}^{-L(E_1-E_0)}\big)\Big] \tag{47}$$

where $E_1 = \frac{3}{2}\Omega$ and $E_1 = \frac{5}{2}\Omega$. The ground state denoted by $|0\rangle$ corresponds to the lowest eigenvalue E_0 of $\hat{\mathcal{H}}$ and is assumed to be unique and separated by a gap from E_1. As $L \to \infty$, this expression is dominated by the ground state. The term $\mathrm{tr}\,\exp(-L\hat{\mathcal{H}})$ can be easily computed to yield the stationary phase condition, i.e., $\sqrt{\frac{\lambda l_\mathrm{p}}{2}} = \frac{3}{4}$. Introducing $\hat{\mathbf{U}}(s)$, the interaction representation of the operator $\hat{\mathbf{u}}$,

$$\hat{\mathbf{U}}(s) = \mathrm{e}^{-s\hat{\mathcal{H}}}\,\hat{\mathbf{u}}\,\mathrm{e}^{s\hat{\mathcal{H}}} \tag{48}$$

we can express the correlation of $\mathbf{u}$ as

$$\langle \mathbf{u}(s)\cdot\mathbf{u}(s')\rangle = \frac{\mathrm{tr}[\hat{\mathbf{U}}(s)\cdot\hat{\mathbf{U}}(s')c\,\mathrm{e}^{-L\hat{\mathcal{H}}}]}{\mathrm{tr}\,\mathrm{e}^{-L\hat{\mathcal{H}}}}, \qquad 0 \leq s \leq s' \leq L. \tag{49}$$

As $L \to \infty$, the ground state is dominant in the above expression contribution:

$$\langle \mathbf{u}(s)\cdot\mathbf{u}(s')\rangle = \langle 0|\mathcal{T}\hat{\mathbf{U}}(s)\cdot\hat{\mathbf{U}}(s')|0\rangle \tag{50}$$

where $\mathcal{T}$ is a time ordering operator. In general, the correlation functions of the statistical analog correspond with the time-ordered products of the corresponding quantum fields. If we use the basis $|\mathbf{n}\rangle$ in which $\hat{\mathcal{H}}$ is diagonal, the correlation can be further simplified to yield

$$
\begin{aligned}
\langle \mathbf{u}(s')\cdot\mathbf{u}(s)\rangle &= \langle 0|\hat{\mathbf{u}}\mathrm{e}^{-|s'-s|\hat{\mathcal{H}}}\,\hat{\mathbf{u}}\,\mathrm{e}^{|s'-s|\hat{\mathcal{H}}}|0\rangle \\
&= \sum_{\mathbf{n}}|\langle 0|\hat{\mathbf{u}}|\mathbf{n}\rangle|^2\mathrm{e}^{-(E_{\mathbf{n}}-E_0)|s'-s|} \\
&= \mathrm{e}^{-(E_1-E_0)|s'-s|} \\
&= \mathrm{e}^{-|s'-s|/l_0}.
\end{aligned} \tag{51}
$$

As we have seen, the operator representation of the free energy are especially useful for a very long chain. In general, we can make ground state dominance approximation for a long chain as long as the Hamiltonian of the statistical analog $\hat{\mathcal{H}}$ is hermitian bounded below and

has a discrete energy spectrum. In this case, the free energy per unit length is approximately equal to the ground state energy of $\hat{\mathcal{H}}$. The calculation of the correlation function reduces to calculation of transition amplitudes $\langle 0|\hat{\mathbf{u}}|\mathbf{n}\rangle$. For an ideal semiflexible chain, $\hat{\mathbf{u}}$ connects $\langle 0|$ with the first excited state with non-vanishing transition amplitude, resulting in the correlation function given in Eq. (51).

3 END-TO-END DISTRIBUTION FUNCTION

There have been several studies over the years which have focused on the distribution of end-to-end distance of semiflexible chains. Most of these studies have started by considering the chains near the rod limit and have computed corrections in powers of t^{-1} where t is the ratio of the bare persistence length to the contour length. In general the calculations have been done only to low orders in t^{-1}. These calculations are quite involved, and more importantly, they do not provide reliable results in the interesting cases, i.e., when t is on the order of unity. In a very recent paper Wilhelm and Frey [26] have reported analytic and numerical (Monte Carlo) calculations for the radial distribution function for a range of values t. The analytical expressions are given in terms of an infinite series involving the second Hermite polynomials for chains in three dimensions. The meanfield like theory presented in the previous section can be used to derive a very simple expression for the distribution function of end-to-end distance.

The distribution function of the end-to-end distance R is

$$G(R; L) = \left\langle \delta(\mathbf{R} - \int_0^L \mathbf{u}(s)\mathrm{d}s) \right\rangle \tag{52}$$

where the average is evaluated as

$$\langle \ldots \rangle = \frac{\int \mathcal{D}[\mathbf{u}(s)] \ldots \Psi_{\mathrm{MF}}[\mathbf{u}(s)]}{\int \mathcal{D}[\mathbf{u}(s)] \ \Psi_{\mathrm{MF}}[\mathbf{u}(s)]}. \tag{53}$$

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The weight $\Psi[\mathbf{u}(s)]$ is (see Eq. (9))

$$\Psi[\mathbf{u}(s)] \propto \exp\left[-\frac{l_{\mathrm{p}}}{2}\int_0^L \mathrm{d}s\Big(\frac{\partial\mathbf{u}}{\partial s}\Big)^2\right] \prod_{0\le s\le L}\delta(\mathbf{u}^2(s)-1). \tag{54}$$

Following the previous section, at the level of the stationary phase approximation, the weight can be replaced by

$$\Psi_{\mathrm{MF}}[\mathbf{u}(s)] \propto \exp\left[-\frac{l_{\mathrm{p}}}{2}\int_0^L \mathrm{d}s\Big(\frac{\partial\mathbf{u}}{\partial s}\Big)^2 - \lambda\int_0^L \mathrm{d}s\mathbf{u}^2(s) - \delta(\mathbf{u}_0^2 + \mathbf{u}_L^2)\right]. \tag{55}$$

where $\mathbf{u}_0 = \mathbf{u}(0)$ and $\mathbf{u}_L = \mathbf{u}(L)$. The parameters λ and δ, which are used to enforce the constraint $\mathbf{u}^2(s) = 1$ by a global constraint $\langle\mathbf{u}^2(s)\rangle = 1$, are determined variationally. From the result in sec. 2.2, it is clear that due to chain fluctuations at the ends the global constraint $\langle\mathbf{u}^2(s)\rangle$ cannot be imposed using only one parameter as suggested by others [27]. The variational solutions for λ and δ depend on the problem under consideration. For the calculation of $G(R;L)$ the optimal values of λ and δ are different from that obtained in section 2.

We calculate $G(R;L)$ by replacing the true weight in Eq. (54) by $\Psi_{\mathrm{MF}}[\mathbf{u}(s)]$ given in Eq. (55). The equation for $G(R;L)$ with the weight given by $\Psi_{\mathrm{MF}}[\mathbf{u}(s)]$ is

$$G(R;L) = \mathcal{N}^{-1}\int_{-i\infty}^{i\infty}\frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\int \mathrm{d}\lambda\mathrm{d}\delta\int \mathcal{D}[\mathbf{u}(s)]\, e^{-\mathbf{k}\cdot(\mathbf{R}-\int_0^L \mathrm{d}s\mathbf{u}(s))}\,\Psi_{\mathrm{MF}}[\mathbf{u}(s)] \tag{56}$$

where $\mathcal{N}$ is an appropriate normalization constant. The functional integral over $\mathbf{u}(s)$ in Eq. (56) is done by replacing $\mathbf{u}(s)$ by $\mathbf{u} - \frac{\mathbf{k}}{2\lambda}$. The resulting path integral corresponds to a harmonic oscillator that makes a transition from $\mathbf{u}_0 - \frac{\mathbf{k}}{2\lambda}$ to $\mathbf{u}_L - \frac{\mathbf{k}}{2\lambda}$ in "time" L. Using the standard result for harmonic oscillator propagator the distribution function $G(R;L)$ becomes

$$G(R;L) = \int \mathrm{d}\lambda\int \mathrm{d}\delta\, \exp\big\{-\mathcal{F}[\lambda,\delta]\big\} \tag{57}$$

where

$$\mathcal{F}[\lambda,\delta] = \frac{3}{2}\left[\ln\Big(\frac{L\lambda+2\delta}{4\lambda^2}\Big) + \ln\Big(\frac{\sinh\Omega L}{\Omega L}\Big) + \ln(\alpha\beta)\right] - \lambda L - 2\delta + \frac{R^2\lambda^2}{\lambda L+2\delta} + \frac{\alpha}{\beta}, \tag{58}$$

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with

$$\alpha = \delta + l_{\mathrm{p}}\Omega \coth\left(\frac{\Omega L}{2}\right), \tag{59}$$

$$\beta = \delta + \frac{l_{\mathrm{p}}\Omega}{2}\tanh\left(\frac{\Omega L}{2}\right) + \frac{1}{\lambda L + 2\delta}, \tag{60}$$

and

$$\Omega = \sqrt{\frac{2\lambda}{l_{\mathrm{p}}}}. \tag{61}$$

We evaluate the integrals over λ and δ (see Eq. (57)) by the stationary phase approximation. This approximation replaces the constraint $\mathbf{u}^2(s) = 1$ by a global constraint $\langle \mathbf{u}^2(s) \rangle = 1$. If the global constraint is enforced using only one variational parameter, as suggested elsewhere [27], then one simply obtain the incorrect Gaussian expression for $G(R; L)$. The presence of the parameter δ accounts for the suppression of the fluctuations of the ends of the chain. The stationarity condition

$$\frac{\partial}{\partial\lambda}\mathcal{F}[\lambda, \delta] = 0 \tag{62}$$

gives, after some algebra,

$$\sqrt{\frac{\lambda l_{\mathrm{p}}}{2}} = \frac{3}{4}\left(\frac{1}{1 - \frac{R^2}{L^2}}\right) \tag{63}$$

and we find that δ does not show any significant variation with R. Using the stationary values of λ and δ the distribution of the end-to-end distance for the semiflexible chain becomes

$$G(R; L) = \mathrm{const}\frac{1}{(1 - \frac{R^2}{L^2})^{9/2}} \exp\left[-\frac{9L}{8l_{\mathrm{p}}}\frac{1}{(1 - \frac{R^2}{L^2})}\right]. \tag{64}$$

We showed in the previous section that within the stationary phase approach, which enforces thae constraint only globally, the persistence length is reduced to $l_0 = \frac{2}{3}l_{\mathrm{p}}$ instead of l_p. If we let $t = \frac{L}{l_0}$ the radial probability density in three dimensions for semiflexible chains is given by the simple expression, namely,

$$P(r; t) = 4\pi\mathcal{C}\frac{r^2}{(1 - r^2)^{9/2}}\exp\left[-\frac{3t}{4}\frac{1}{(1 - r^2)}\right] \tag{65}$$

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where $r = \frac{R}{L}$. The normalization constant $\mathcal{C}$ which is determined using the condition

$$\int_0^1 \mathrm{d}r P(r;t) = 1 \tag{66}$$

and is given by

$$\mathcal{C} = \frac{1}{\pi^{3/2}\mathrm{e}^{-\alpha}\alpha^{-3/2}(1 + 3\alpha^{-1} + \frac{15}{4}\alpha^{-2})} \tag{67}$$

where $\alpha = 3t/4$.

The distribution function, $P(r;t)$, goes as r^2 as $r \to 0$ and vanishes at $r = 1$. The peak of the distribution function occurs at

$$r_{\max} = \sqrt{\frac{\eta + \sqrt{\eta^2 + 14}}{7}} \tag{68}$$

where $\eta = \frac{5}{2} - \frac{3}{4}t$. In Fig. (1) we plot $P(r;t)$ for the five values of t for which Wilhelm and Frey [26] have presented simulation data. We find that our simple expression in Eq. (64) almost quantitatively reproduces the data with the maximum deviation of about 10% at the peak for $t = 0.5$.

We have also calculated the first two moments of the distribution function and find that they reproduce the exact results in both the random coil limit and the rod limit. The distribution function $P(r;t)$ also has the correct limiting behavior ($\sim \delta(1-r)$) as $t \to 0$. Thus the meanfield variational approach yields a simple expression for $P(r;t)$ that is in quantitative agreement with simulation and hence can form the basis to analyze experiments.

4 SEMIFLEXIBLE CHAINS UNDER TENSION

The meanfield theory described in the previous section is especially useful when one encounters semiflexible chains in the presence of fields for which tractable calculations are difficult. In this section we use the variational theory to investigate the external field on

the conformational properties of a semiflexible chain. Even though the analogous problems in flexible chains was extensively studied, the corresponding problems in the semiflexible chains has only recently attracted much attention [27-32]. The earliest theoretical paper dealing with this problem was initiated by Fixman and Kovacs [28]. These authors used a modified version of the Gaussian model for stiff chains and provided expressions for the stretching as a function of applied force. Their treatment is only valid when the applied force is small and significant deviation from these predictions are observed at sufficiently large values of the external force. Marko and Siggia [31-32] have calculated the extension as a function of force for wormlike chains and found that their results fit the experimental data very well. Some aspects of this theory have also been considered by Odijk [29] who also discusses the competition between entropically dominated effects and elasticity effects. The meanfield type approach adopted here is, we believe, more general than those adopted in the literature.

Gaussian chains can be arbitrarily extended under tension f as implied by Hook's law of elastic response, i.e., $R \sim Llf$; real chains cannot be extended beyond the contour length L. As the magnitude of tension exerted on both ends of a semiflexible chain increases one expects an interesting crossover to occur from Hook's limit to fully extended limit ($R = L$). Thus the problem of stretched semiflexible chains entails a competition between entropy dominated effects and ordering due to the external field $\mathbf{f}$. We will show that the meanfield treatment quantitatively reproduces experiments on DNA [5] thus providing further evidence for the validity of meanfield approach.

4.1 Stationary phase condition

For mathematical convenience, we will adopt translationally symmetric chain model introduced in Eq. (38). Each segment in a semiflexible chain is assumed to be stretched by

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tangential force $\mathbf{f}(s)$ which tends to suppress chain fluctuations. The weight for the case of semiflexible chains in the presence of the stretching is

$$\Psi[\mathbf{u}(s), \lambda(s)] \propto \exp\left[-\tfrac{1}{2} \int_0^L \int_0^L \mathrm{d}s\mathrm{d}s' \mathbf{u}(s)Q(s, s')\mathbf{u}(s') + \int_0^L \mathbf{u}(s) \cdot \mathbf{f}(s)\mathrm{d}s\right] \tag{69}$$

where Q is the same operator as introduced in Eq. (39), i.e.,

$$Q(s, s') = \left[-l_\mathrm{p}\left(\frac{\partial}{\partial s}\right)^2 + 2\lambda\right]\delta(s' - s). \tag{70}$$

The last term in the exponent is the energy penalty for chain conformations which are not parallel to $\mathbf{f}(s)$. The free energy can be written as

$$
\begin{aligned}
\exp(-F/k_\mathrm{B}T) &\propto \int_{-i\infty}^{i\infty} \mathcal{D}[\lambda(s)] \int \mathcal{D}[\mathbf{u}(s)]\, \mathrm{e}^{\int_0^L \lambda(s)\mathrm{d}s}\, \Psi[\mathbf{u}(s), \lambda(s)] \\
&\propto \int_{-i\infty}^{i\infty} \mathcal{D}[\lambda(s)]\exp\left\{-\mathcal{F}[\lambda(s), \mathbf{f}(s)]\right\}
\end{aligned} \tag{71}
$$

where $\mathcal{F}$ is the free energy functional given by

$$\mathcal{F}[\lambda(s), \mathbf{f}(s)] = -\ln \int \mathcal{D}[\mathbf{u}(s)]\Psi[\mathbf{u}(s), \lambda(s)] - \int_0^L \lambda(s)\mathrm{d}s + \mathrm{const.}. \tag{72}$$

Integration with respect to $\mathbf{u}(s)$ yields

$$
\begin{aligned}
\mathcal{F}[\lambda(s), \mathbf{h}(s)] &= \tfrac{3}{2}\, \mathrm{tr}\, \ln Q - \tfrac{1}{2} \int_0^L \int_0^L \mathbf{f}(s)Q^{-1}(s, s')\mathbf{f}(s') \\
&\quad - \int_0^L \lambda(s)\mathrm{d}s + \mathrm{const.}.
\end{aligned} \tag{73}
$$

Note that $\mathcal{F}[\lambda(s), \mathbf{f}(s)]$ is the generating functional for the connected correlation function defined by

$$
\begin{aligned}
\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle_\mathrm{c} &= -\frac{\delta}{\delta\mathbf{f}(s)} \cdot \frac{\delta\mathcal{F}}{\delta\mathbf{f}(s')} \\
&= \frac{\partial}{\delta\mathbf{f}(s)} \cdot \langle \mathbf{u}(s') \rangle \\
&= \langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle - \langle \mathbf{u}(s) \rangle \cdot \langle \mathbf{u}(s') \rangle.
\end{aligned} \tag{74}
$$

As $\mathbf{f}$ goes to zero, $\langle \mathbf{u}(s) \rangle$ vanishes. In this case, the distinction between the connected correlation function and the correlation function disappears. Performing the functional differentiations in Eq. (46), we get

$$\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle_\mathrm{c} = 3Q^{-1}(s, s') \tag{75}$$

and

$$\langle \mathbf{u}(s) \rangle = -\frac{\delta \mathcal{F}}{\delta \mathbf{f}(s)} = \int_0^L Q^{-1}(s, s') \mathbf{f}(s'). \tag{76}$$

Integrations of each term in Eq. (74) with respect to s and s' lead to the following expression for ΔR^2

$$
\begin{aligned}
\Delta R^2 &= \langle R^2 \rangle - \langle R \rangle^2 \\
&= \int_0^L \int_0^L \langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle \mathrm{d}s \mathrm{d}s' - \int_0^L \int_0^L \langle \mathbf{u}(s) \rangle \cdot \langle \mathbf{u}(s') \rangle \mathrm{d}s \mathrm{d}s' \\
&= \int_0^L \int_0^L \frac{\delta}{\delta \mathbf{f}(s)} \cdot \frac{\delta \mathcal{F}}{\delta \mathbf{f}(s')} \mathrm{d}s \mathrm{d}s'.
\end{aligned} \tag{77}
$$

All relevant quantities can be thus expressed in terms of the free energy functional $\mathcal{F}[\lambda(s), \mathbf{f}(s)]$.

Following the general formalism described in section 2, the case of ideal semiflexible chains, the free energy is approximated by the minimum value of the corresponding free energy functional which occurs along the stationary phase trajectory λ. The stationary phase condition is obtained by requiring $\frac{\delta}{\delta \lambda(s)} \mathcal{F} = 0$. To this end, we first note that

$$
\begin{aligned}
\frac{\delta}{\delta \lambda(s)} \mathrm{tr} \ln Q &= \frac{\delta}{\delta \lambda(s)} \sum_{s'} (\ln Q)(s', s') \\
&= 2 \, Q^{-1}(s, s).
\end{aligned} \tag{78}
$$

and

$$\frac{\delta}{\delta \lambda(s)} Q^{-1}(s', s'') = 2 \, Q^{-1}(s', s) Q^{-1}(s, s''). \tag{79}$$

The stationary phase condition leads to

$$1 = \tfrac{3}{2} \left(\frac{2}{Q} \right)_{s,s} + \int_0^L \int_0^L \mathrm{d}s' \mathrm{d}s'' \mathbf{f}(s') Q^{-1}(s', s) Q^{-1}(s, s'') \mathbf{f}(s''). \tag{80}$$

The stationary phase value $\lambda(s)$ thus depends on the value of the external force $\mathbf{f}(s)$. The simplest but nontrivial case corresponds to the case of $\mathbf{f}(s) = \mathbf{f} = \mathrm{const}$. It is the case of stretching of semiflexible chains under constant value of $\mathbf{f}$ that is appropriate to the recent experiments on DNA [5]. If $\mathbf{f}$ is uniform, then so is λ. In this case the stationary phase

condition reduces to

$$
\begin{aligned}
1 &= \tfrac{3}{2}\left(\frac{1}{-\frac{l_\mathrm{p}}{2}(\frac{\partial}{\partial s'})^2 + \lambda}\right)_{s,s'} + \frac{f^2}{4\lambda^2} \\
&= \tfrac{3}{2}\sum_{-\infty}^{\infty}\frac{1}{\lambda L + \frac{l_\mathrm{p}}{2}\frac{(2\pi n)^2}{L}} + \frac{f^2}{4\lambda^2}.
\end{aligned}
\tag{81}
$$

With the aid of Eq. (33), this can be written in a closed form

$$
1 = \tfrac{3}{4}\sqrt{\frac{2}{l_\mathrm{p}\lambda}}\,\coth(\tfrac{1}{2}\Omega L) + \frac{f^2}{4\lambda^2}
\tag{82}
$$

where $\Omega = \sqrt{\frac{2\lambda}{l_\mathrm{p}}}$. As $L \to \infty$, this equation can be further simplified to yield

$$
1 - \tfrac{3}{4}\sqrt{\frac{2}{l_\mathrm{p}\lambda}} = \frac{f^2}{4\lambda^2}.
\tag{83}
$$

As $f \to 0$, this equation reduces to the earlier one in Eq. (21) as expected.

4.2 Conformation of a semiflexible chain under tension

In the case of uniform $\mathbf{f}$, we obtain a simple expression for the correlation function:

$$
\begin{aligned}
\langle \mathbf{u}(s)\cdot\mathbf{u}(s')\rangle &= 3Q^{-1}(s,s') + \frac{f^2}{4\lambda^2} \\
&= \tfrac{3}{2}\sum_{-\infty}^{\infty}\frac{\exp[i\frac{2\pi n}{L}|s'-s|]}{\lambda L + \frac{l_\mathrm{p}}{2}\frac{(2\pi n)^2}{L}} + \frac{f^2}{4\lambda^2} \\
&= \tfrac{3}{4}\sqrt{\frac{2}{l_\mathrm{p}\lambda}}\,\frac{\cosh[(L-2|s'-s|)\Omega/2]}{\sinh(\Omega L/2)} + \frac{f^2}{4\lambda^2}.
\end{aligned}
\tag{84}
$$

where $\Omega = \sqrt{\frac{2\lambda}{l_\mathrm{p}}}$. To derive the last step from the previous one, we used Eq. (33). As $L \to \infty$, the above equation can be further simplified to yield

$$
\langle \mathbf{u}(s)\cdot\mathbf{u}(s')\rangle = \tfrac{3}{4}\sqrt{\frac{2}{l_\mathrm{p}\lambda}}\,\mathrm{e}^{-|s'-s|\Omega} + \frac{f^2}{4\lambda^2}.
\tag{85}
$$

If we set $|s'-s|$ to zero, this equation reduces to the stationary phase condition. Thus the free energy minimization condition in this case also amounts to requiring $\mathbf{u}^2(s) = 1$. As

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$\mathbf{f} \to 0$, the coefficient in the exponential function becomes 1, resulting in the same expression as in Eq. (51).

Using the correlation function in Eq. (85), the mean squared internal distance of the chain under tension can be obtained

$$
\begin{aligned}
\langle |\mathbf{r}(s') - \mathbf{r}(s)|^2 \rangle &= \int_s^{s'} \int_s^{s'} \langle \mathbf{u}(s_1) \cdot \mathbf{u}(s_2) \rangle \mathrm{d}s_1 \mathrm{d}s_2 \\
&= \tfrac{3}{4} \sqrt{\frac{2}{l_\mathrm{p}\lambda}} \Big[\frac{2}{\Omega} |s' - s| - \frac{2}{\Omega^2} (1 - \mathrm{e}^{-\Omega|s'-s|}) \Big] + \frac{f^2}{4\lambda^2} (s' - s)^2.
\end{aligned} \tag{86}
$$

We can easily see that, for small $|s' - s|$, the first two term on the R.H.S. of Eq. (86) is dominant. As $|s' - s|$ becomes larger, the last term is more important. At large length scales, the chain conformation is thus mainly determined by the orienting field. We can now introduce a crossover length S_f at which these two length scales coincide. If the crossover occurs at S_f which is somewhat larger than Ω^{-1}, then we can get a simple expression for S_f; this can be obtained by balancing the first term with the last one in R.H.S of Eq. (86)

$$
S_f = \tfrac{3}{4} \sqrt{\frac{2}{l_\mathrm{p}\lambda}} \Big(\frac{4}{f^2} \frac{\lambda^2}{\Omega} \Big). \tag{87}
$$

The condition, $S_f \gg \Omega^{-1}$, is equivalent to $\frac{f^2}{4\lambda^2} \ll \tfrac{3}{4} \sqrt{\frac{2}{l_\mathrm{p}\lambda}} = \mathcal{O}(1)$ or $fl_\mathrm{p} \ll 1$. Under this condition, the stationary phase condition coincides with that for an ideal semiflexible chain. This results in

$$
S_f \sim \frac{1}{f^2 l_\mathrm{p}}. \tag{88}
$$

The longitudinal size corresponding to S_f is called a *tensile screening length*, [34] and is denoted by ξ_f. By noting that parts of the chain within the length scale S_f resemble an ideal chain, we can have

$$
\xi_f \sim f^{-1}. \tag{89}
$$

The condition $\frac{f^2}{4\lambda^2} \ll 1$ for the above expression to be valid in turn amounts to requiring $fl_\mathrm{p} \ll 1$ or equivalently $\xi_f \gg l_\mathrm{p}$. It is interesting to note that results for S_f and ξ_f given above are the same as those for a Gaussian chain under tension. This can be understood

as follows; the condition, $\xi_f \gg l_{\mathrm{p}}$, for the above results to be valid, is equivalent to saying that the tensile screening length ξ_f contains large number of chain segments of length l_{p}. The chain stiffness becomes marginal in determining the shape of parts of chains within the length scale ξ_f. Since the effect of $\mathbf{f}$ is important only beyond this length scale, the chain stiffness is not "coupled" to the external field $\mathbf{f}$.

As $\frac{f^2}{4\lambda^2}$ becomes much larger than $\frac{3}{4}\sqrt{\frac{2}{l_{\mathrm{p}}\lambda}}$ or equivalently $fl_{\mathrm{p}} \to \infty$ and thus S_f approaches 0. This implies that, at any length scale beyond $S_f \approx 0$, the chain conformation is governed by the interaction term $-\int \mathbf{f} \cdot \mathbf{u}(s)$. As we will see below, as $l_{\mathrm{p}}f \to \infty$, the entropical contribution is not balanced by the energy penalty for crumpled conformation. That is the chain segments are aligned with $\mathbf{f}$ as expected. These quantitative considerations, which were already implicit in the calculations of Fixman and Kovacs [28], can be made quantitative using our general formalism.

4.3 Elastic response of a semiflexible chain

Let us now consider the average elongation z defined by

$$z = \left\langle \int_0^L \mathrm{d}s \mathbf{u}(s) \cdot \frac{\mathbf{f}}{f} \right\rangle. \tag{90}$$

This quantity, which is experimentally measureable, shows how the chain responses to the tangential field. The statistical average in Eq. (90) can be conveniently expressed in terms of the free energy functional $\mathcal{F}$ (see Eq. (73)). For the case of uniform $\mathbf{f}$, we obtain a simple expression for this:

$$
\begin{aligned}
z = \frac{\mathbf{f}}{f} \cdot \frac{\delta \mathcal{F}}{\delta \mathbf{f}} &= f \int_0^L \left[-l_{\mathrm{p}} \left(\frac{\delta}{\delta s} \right)^2 + 2\lambda \right]^{-1} \mathrm{d}s \\
&= f \frac{L}{2\lambda(f)}.
\end{aligned}
\tag{91}
$$

where the argument in $\lambda(f)$ is introduced to emphasize the dependence of λ on f. This equation along with the stationary phase condition Eq. (83) provide the average elongation

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with respect to f. To obtain analytic expressions, we first take two limiting cases of $l_{\mathrm{p}} \to 0$ and $f \to \infty$. As $l_{\mathrm{p}} \to 0$ or more precisely $l_{\mathrm{p}}f \to 0$, the problem reduces to that of a stretched Gaussian chain as mentioned in sec. 4.1. In this case, we can get the following elastic response relation

$$z = f\frac{R_0^2}{3} \tag{92}$$

where $R_0^2 = 2l_0 L = 2(\frac{2}{3}l_{\mathrm{p}})L$ is the size of the corresponding ideal semiflexible chain. This is the elastic response relation of a Gaussian chain under tension [35]. For the case of $fl_{\mathrm{p}} \ll 1$, the stationary phase condition can be expanded in terms of f^2. Up to f^2, we get

$$\lambda(h) \approx \lambda + \frac{f^2}{2\lambda} \tag{93}$$

where λ is the stationary phase condition for $f = 0$. Thus the average elongation is given by

$$z \approx f\frac{R_0^2}{3}[1 - \tfrac{8}{9}f^2 l_0^2]. \tag{94}$$

Note here that the control parameter in this expansion is fl_{p} (or fl_0).

As l_{p} increases the term $\frac{f^2}{4\lambda^2}$ in the stationary phase condition becomes important. If the value of l_{p} reaches the same order of magnitude as that of ξ_f, we expect the effect of the orienting field to be important over all length scales. In other words, chain fluctuations become frozen as $l_{\mathrm{p}}f$ becomes large. As $f \to \infty$, the stationary phase condition has a solution at $\lambda^{-1} = 0$, resulting in $\lambda = \frac{1}{2}f$. The average elongation is thus given by $z = L$. Chain fluctuation are totally suppressed in this case. For finite but much larger f than l_{p}, $\lambda(f)$ can be approximated as

$$\lambda(f) = \tfrac{1}{2}f\Big(1 + \tfrac{3}{4}\sqrt{\frac{1}{l_{\mathrm{p}}f}}\Big). \tag{95}$$

Accordingly z for finite f is smaller than L, which is due to chain fluctuations.

$$z \approx L\Big(1 - \tfrac{3}{4}\sqrt{\frac{1}{l_{\mathrm{p}}f}}\Big). \tag{96}$$

Similar result with slightly larger numerical factor was obtained by T. Odijk [29] considering a semiflexible chain near the rod limit.

Since the chain under strong elongation as described by Eq. (96) is nearly parallel to the orienting force $\mathbf{f}$, we can approximate z as

$$
\begin{aligned}
z &= \left\langle \int_0^L \mathbf{u}(s)\mathrm{d}s \cdot \frac{\mathbf{f}}{f} \right\rangle \\
&= \left\langle \int_0^L \cos\theta_f(s)\mathrm{d}s \right\rangle \\
&= L\left[1 - \tfrac{1}{2}\langle\theta_f^2(s)\rangle\right]
\end{aligned}
\tag{97}
$$

where $\theta(s)$ is the angle between $\mathbf{f}$ and $\mathbf{u}(s)$. For a uniform field, we expect $\langle\theta_f^2(s)\rangle$ not to depend on s for a long chain, i.e., $\langle\theta_f^2(s)\rangle = \langle\theta_f^2\rangle$. Comparing Eq. (96) and (97), we can obtain the expression for this quantity:

$$
\langle\theta_f^2\rangle = \tfrac{3}{2}\sqrt{\frac{1}{l_\mathrm{p}f}}.
\tag{98}
$$

This result again differs by numerical factor from the corresponding expression for $\langle\theta_f^2\rangle$ derived by Odijk [29].

In the above analysis, we have seen that the stationary phase approach reproduces results consistent with literature in limiting cases. To test our theory further, we solved the stationary phase condition numerically. To compare with experimental data obtained by Smith et al. [5] on the stretching of DNA (see also Fig. 2 in Ref. [32]) l_0 and L have been chosen to be 53.4nm and 32.80μm respectively. In Fig. 2, z/L is plotted against $\ln f$. Our numerical solution (continuous curve) is well in quantitative agreement with the experimental data [5].

In the previous analysis, we have seen that a strong orienting field tends to suppress chain fluctuations as is implied by the correlation and the elastic response relation. This is also manifested in the ratio $\frac{\Delta R^2}{\langle R^2 \rangle}$. Using Eq. (77), we get

$$
\Delta R^2 = \tfrac{3}{4}\sqrt{\frac{2}{l_\mathrm{p}\lambda}}\left[\frac{2}{\Omega}L - \frac{2}{\Omega^2}(1 - \mathrm{e}^{-\Omega L})\right].
\tag{99}
$$

and thus

$$
\frac{\Delta R^2}{\langle R^2 \rangle} = \frac{\Delta R^2}{\Delta R^2 + \frac{f^2 L^2}{4\lambda^2}}.
\tag{100}
$$

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For a short chain, $\frac{\Delta R^2}{<R^2>} = \mathcal{O}(1)$ while it approaches zero as $L \to \infty$. It can be easily seen that value of this quantity crosses over at the contour length $L \approx S_f$ from fluctuation dominated limit ($\frac{\Delta R^2}{<R^2>} = \mathcal{O}(1)$) to fluctuation suppressed limit ($\frac{\Delta R^2}{<R^2>} \approx 0$). As $l_\mathrm{p} f \to \infty$, S_f approaches zero. Thus in this case, chain fluctuation becomes totally suppressed for a chain with contour length $L \gg S_f \approx 0$.

4.4 Operator representation

Just as in the case of an ideal semiflexible chain, it is instructive to use operator representation of the free energy functional $\mathcal{F}[\lambda, \mathbf{f}]$. The corresponding Hamiltonian in this case describes a quantum harmonic oscillator in the linear force field described by $\mathbf{f}$:

$$
\begin{aligned}
\hat{\mathcal{H}}[\lambda, \mathbf{f}] &= \hat{\mathcal{H}}[\lambda] + \Delta\hat{\mathcal{H}} \\
&\equiv \frac{\hat{\mathbf{p}}^2}{2l_\mathrm{p}} + \lambda\hat{\mathbf{u}}^2 - \hat{\mathbf{u}} \cdot \mathbf{f} \\
&= \frac{\hat{\mathbf{p}}^2}{2l_\mathrm{p}} + \lambda\left(\hat{\mathbf{u}} - \frac{\mathbf{f}}{2\lambda}\right)^2 - \frac{f^2}{4\lambda}.
\end{aligned}
\tag{101}
$$

Since $[\hat{\mathbf{p}}, \mathbf{f}] = 0$ and thus the commutator $[\hat{p}_j, \hat{u}_k] = -i\delta_{jk}$ is invariant under $\hat{\mathbf{u}} \to \hat{\mathbf{u}} - \frac{\mathbf{f}}{2\lambda}$, the external field just shifts eigenvalues of $\hat{\mathcal{H}}[\lambda, \mathbf{f}]$ by the same amount $-\frac{f^2}{4\lambda}$. This results in

$$
\mathrm{tr}\, e^{-L\hat{\mathcal{H}}[\lambda, \mathbf{f}]} = \left(\frac{1}{2\sinh(\frac{1}{2}\Omega L)}\right)^3 \exp\left(\frac{f^2}{4\lambda}L\right).
\tag{102}
$$

This leads to the same stationary phase condition as in Eq. (83).

Correlation function of $\mathbf{u}(s)$ can be also computed following the similar steps to that leading to Eq. (51)

$$
\begin{aligned}
\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle &= \sum_{\mathbf{n}} \left|\langle 0|\left(\hat{\mathbf{u}} + \frac{\mathbf{f}}{2\lambda}\right)|\mathbf{n}\rangle\right|^2 e^{-(E_\mathbf{n} - E_0)|s' - s|} \\
&= |\langle 0|\hat{\mathbf{u}}|\mathbf{n}\rangle|^2\, e^{-(E_1 - E_0)|s' - s|} + \frac{f^2}{4\lambda^2} \\
&= \frac{3}{4}\sqrt{\frac{2}{l_\mathrm{p}\lambda}}\, e^{-|s' - s|\Omega} + \frac{f^2}{4\lambda^2}.
\end{aligned}
\tag{103}
$$

29

The operator representation again produces the same result as the functional integral formalism. One of the advantages of using the operator representation is that we can use ground state dominance approximation provided there is a energy gap.

5. SEMIFLEXIBLE CHAINS IN A NEMATIC FIELD

As a final example of the utility of our approach we consider an semiflexible chain in a nematic environment. These calculations expose conditions under which the stationary phase approach is not successful. The interaction energy of a chain in a nematic field along $\mathbf{n}$ is assumed to be $-g \int_0^L [\mathbf{u}(s) \cdot \mathbf{n}]^2$, where the coupling constant g measures the strength of nematic field. Thus conformations of nematic polymers either parallel or anti-parallel to the nematic field are equally energetically favorable. This is in contrast to the case of a stretched chain. The Hamiltonian of a single chain in the present case is given by [9, 36]

$$\frac{\mathcal{H}[g]}{k_{\mathrm{B}}T} = \int_0^L \mathrm{d}s \left\{ \frac{l_{\mathrm{p}}}{2} \left(\frac{\partial \mathbf{u}}{\partial s} \right)^2 - g[\mathbf{u}(s) \cdot \mathbf{n}]^2 \right\} \tag{104}$$

where $\mathbf{u}(s)$ is defined only on a unit sphere of $|\mathbf{u}(s)| = 1$. At the meanfield level this takes the form

$$\frac{\mathcal{H}[\lambda, g]}{k_{\mathrm{B}}T} = \frac{1}{2} \int_0^L \int_0^L \mathrm{d}s \mathrm{d}s' \, \mathbf{u}(s) \, Q(s, s') \, \mathbf{u}(s') - g \int_0^L \mathrm{d}s \, \mathbf{u}_z^2(s) \tag{105}$$

such that the weight is given by

$$\Psi_{\mathrm{MF}}[\mathbf{u}(s), g] \propto \exp \left\{ -\frac{\mathcal{H}[\lambda, g]}{k_{\mathrm{B}}T} \right\} \tag{106}$$

where the direction of the nematic field is chosen to be parallel to z-axis. With the convention $\mathbf{u}_\perp = (u_x, u_y, 0)$, this can be rewritten as

$$\frac{\mathcal{H}[\mathbf{u}(s)]}{k_{\mathrm{B}}T} = \frac{1}{2} \int_0^L \int_0^L \mathrm{d}s \mathrm{d}s' \left[\mathbf{u}_\perp(s) \, Q(s, s') \, \mathbf{u}_\perp(s') + u_z(s) \, Q_1(s, s') \, u_z(s') \right] \tag{107}$$

where

$$Q(s, s') = \left[-l_{\mathrm{p}} \left(\frac{\partial}{\partial s} \right)^2 + 2\lambda \right] \delta(s' - s) \tag{108}$$

and

$$Q_1(s, s') = \left[-l_{\mathrm{p}} \left(\frac{\partial}{\partial s} \right)^2 + 2(\lambda - g) \right] \delta(s' - s). \tag{109}$$

The corresponding generating functional $\mathcal{F}[\lambda, g, \mathbf{f}(s)]$, up to an additive constant, now has the following form

$$\begin{aligned}
\mathcal{F}[\lambda, g] &= \mathrm{tr} \ln Q - \frac{1}{2} \int_0^L \int_0^L \mathrm{d}s \mathrm{d}s' \mathbf{f}_\perp(s) Q^{-1}(s, s') \mathbf{f}_\perp(s') \\
&\quad + \frac{1}{2} \mathrm{tr} \ln Q_1 - \frac{1}{2} \int_0^L \int_0^L \mathrm{d}s \mathrm{d}s' f_z(s) Q_1^{-1}(s, s') f_z(s') - \int_0^L \lambda(s) \mathrm{d}s
\end{aligned} \tag{110}$$

from which we can obtain

$$\begin{aligned}
\langle \mathbf{u}_\perp(s) \cdot \mathbf{u}_\perp(s') \rangle &= -\frac{\delta}{\delta \mathbf{f}_\perp(s)} \cdot \frac{\delta \mathcal{F}}{\delta \mathbf{f}_\perp(s')} + \langle \mathbf{u}_\perp(s) \rangle \cdot \langle \mathbf{u}_\perp(s') \rangle \\
&= \frac{1}{2} \sqrt{\frac{2}{l_{\mathrm{p}} \lambda}} \, \mathrm{e}^{-|s' - s|\Omega}
\end{aligned} \tag{111}$$

and

$$\begin{aligned}
\langle u_z(s) \cdot u_z(s') \rangle &= -\frac{\delta}{\delta f_z(s)} \cdot \frac{\delta \mathcal{F}}{\delta f_z(s')} + \langle u_z(s) \rangle \cdot \langle u_z(s') \rangle \\
&= \frac{1}{4} \sqrt{\frac{2}{l_{\mathrm{p}}(\lambda - g)}} \, \mathrm{e}^{-|s' - s|\Omega_1}
\end{aligned} \tag{112}$$

with $\Omega = \sqrt{\frac{2\lambda}{l_{\mathrm{p}}}}$ and $\Omega_1 = \sqrt{\frac{2(\lambda - g)}{l_{\mathrm{p}}}}$. In the last steps of above equations, we set $\mathbf{f}(s)$ to zero. The stationary phase value of λ now satisfies the following equality

$$1 = \frac{1}{2} \sqrt{\frac{2}{l_{\mathrm{p}} \lambda}} + \frac{1}{4} \sqrt{\frac{2}{l_{\mathrm{p}}(\lambda - g)}} \tag{113}$$

which ensures

$$1 = \langle \mathbf{u}_\perp^2(s) \rangle + \langle u_z(s) \rangle = \langle \mathbf{u}^2(s) \rangle. \tag{114}$$

It can be easily seen that the stationary phase value of λ in this case is larger than that for the case of free chains. But $(\lambda - g)$ is smaller than that for the latter case. This implies

that the nematic field induces ordering along the field but decrease the persistence length perpendicular to it. That is

$$
\begin{aligned}
\langle R_\perp^2 \rangle &= \int_0^L \int_0^L \langle \mathbf{u}_\perp(s) \cdot \mathbf{u}_\perp(s') \rangle \mathrm{d}s \mathrm{d}s' \\
&= \tfrac{2}{3}(2l_{\mathrm{eff}}^\perp L) \\
&< \tfrac{2}{3}(2l_0 L) \tag{115}
\end{aligned}
$$

and

$$
\begin{aligned}
\langle R_z^2 \rangle &= \int_0^L \int_0^L \langle u_z(s) \cdot u_z(s') \rangle \mathrm{d}s \mathrm{d}s' \\
&= \tfrac{2}{3}(2l_{\mathrm{eff}}^z L) \\
&< \tfrac{1}{3}(2l_0 L) \tag{116}
\end{aligned}
$$

where $l_0 = \tfrac{2}{3}l_{\mathrm{p}}$ is the persistence length of a free chain. The size of chains in nematic field does not grow as L as $L \to \infty$, as is the case for the stretched chain within the meanfield variational theory. To be more precise, let us consider the stationary phase solutions for two extreme cases. In the following derivations any quantity with (without) argument g corresponds to a nematic polymer (non-interacting polymer).

(a) *The weak nematic limit, $g \to 0$.*

For small g, we can write $\lambda(g) \approx \lambda(1 + \epsilon)$. By assuming both ϵ and g small, we can have

$$
\lambda(g) \approx \lambda(1 + \tfrac{2}{3}gl_0) \tag{117}
$$

and thus

$$
\Omega(g) = \sqrt{2\lambda(g)/l_{\mathrm{p}}} \approx \sqrt{2\lambda/l_{\mathrm{p}}}\,(1 + \tfrac{2}{3}gl_0) \tag{118}
$$

and

$$
\Omega'(g) = \sqrt{2(\lambda(g) - g)/l_{\mathrm{p}}} \approx \sqrt{2\lambda/l_{\mathrm{p}}}\,(1 - \tfrac{1}{3}gl_0). \tag{119}
$$

These lead to

$$
\frac{\langle R_\perp^2 \rangle}{\tfrac{2}{3}(2l_0 L)} \approx 1 - \tfrac{1}{3}gl_0 \tag{120}
$$

32

and

$$\frac{\langle R_z^2 \rangle}{\frac{1}{3}(2l_0 L)} \approx 1 + \tfrac{1}{3}gl_0. \tag{121}$$

Thus the persistence length along the nematic field is increased by the factor of $(1 + \tfrac{1}{3}gl_0)$ which can be compared with $(1 + \tfrac{2}{3}gl_0)$ (in our notation) obtained by Warner at al. [9].

(b) *The strong nematic limit, $g \to \infty$.*

If we simply let $g \to \infty$ in the stationarity condition in Eq. (113), then $\lambda(g)$ and thus $\Omega(g)$ should diverge so that $(\lambda(g) - g)$ remain positive. This results in

$$\langle \mathbf{u}_\perp(s) \cdot \mathbf{u}_\perp(s') \rangle = 0 \tag{122}$$

and

$$\langle u_z(s) \cdot u_z(s') \rangle = \exp(-|s' - s|/2l_{\mathrm{p}}). \tag{123}$$

The diverging nematic field totally suppresses chain fluctuations perpendicular to it but increases the persistence length parallel to it by the factor of 2. The increase of the persistence length along the nematic field by only numerical factor, however, is *not* correct. Several authors predicted an effective persistence which grows exponentially with $\sqrt{gl_{\mathrm{p}}}$ [9, 12, 36, 37]. Following the reference [36], this can be explained as follows; since the interaction energy $-gu_z^2$ which is quadratic in u_z has two minima for $u_z = \pm 1$, the "tunneling" probability from one minimum to the next is very small for large g. This results in the length scale which varies exponentially as $\sqrt{gl_{\mathrm{p}}}$ over which the chain is parallel to the nematic field. For more details see the reference [36].

The stationary phase free energy in Eq. (105) also contains the quadratic interaction term $-gu_z^2$. This term if added to λu_z^2 becomes $(\lambda - g)u_z^2$ with positive $(\lambda - g)$ which has only *one* minimum at $u_z = 0$. Thus the stationary phase approach does not account for the instanton solution, resulting in much smaller persistence length than the exact results. This problem illustrates the possible limitations of the stationary phase approach; if there is a possibility of broken symmetry in the problem then the meanfield variational theory should

be used with caution.

6. CONCLUSIONS

In this chapter we have described a simple meanfield variational approach to study a number of properties of intrinsically stiff chains which are appropriate models for a large class of biopolymers. The exact statistical mechanics of such systems are complicated by the fact that the constraint of the tangent vector being unity has to be enforced at all points along the contour. In the meanfield approach this local constraint, which is difficult to impose, is replaced by a global one. The global constraint ensures that the condition of the tangent vector being unity is obeyed on an average. We have described the calculation of the distribution of end-to-end distance and the elastic response of stiff chains under tension using this basic methodology. In the former example we find that the simple expression almost quantitatively fits the results of simulation. For the case of the stiff chain under tension we recover analytically all the known limits. Furthermore we obtain quantitative agreement with recent experiments on the stretching of DNA using the total contour length and the persistence length as adjustable parameters. The limitations of our approach become obvious in situations that involves broken symmetry such as the case of a stiff chain in a strong nematic potential. Nevertheless it is clear that the meanfield variational approach lays the foundation for systematic studies of more complicated problems involving semiflexible chains.

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